

Resonant Soft X-ray Emission Spectra and Outer Valence Molecular Orbitals of Uranium

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INTRODUCTION

The universality of formation of inner valence molecular orbitals (IVMO) for actinide compounds has been previously examined using x-ray photoelectron spectroscopy (XPS) and fixed energy electron excited x-ray emission spectroscopies.¹⁻⁶ The degree of participation of the IVMO electrons in bonding was rationalized in terms of the physical and chemical properties of the actinide compounds. The correlation of spectral parameters with uranium oxidation state, symmetry of the local uranium environment, and the distance from uranium to nearest neighbors also was established.¹⁻³ However because of resolution constraints, studies of the outer valence molecular orbitals (OVMO) in uranium compounds was not possible.

Third generation VUV/soft x-ray sources make possible obtaining high-resolution resonant x-ray emission spectra (RXES) which have proven to be an efficient tool to study the electronic structure of correlated systems like lanthanides and actinides.⁷⁻¹² The structure of the RXES spectra shows a strong resonant behavior and dependence on the localization degree of the U 5f electrons. For actinide compounds the localization effects for 5f electrons are pronounced.¹⁻³ As an example, in UO₂ the 5f electrons are strongly localized unlike in UO₃, where the 5f electrons participate in the chemical bonding.^{1,2} Resonant valence-to-core x-ray emission spectroscopy makes it possible to directly investigate the U 5f - O 2p electron interaction. Comparative RXES studies of uranium compounds allows assessment of the nature and degree of participation of the U 5f in the chemical bonding. The results of the U 5d near edge x-ray absorption fine structure (NEXAFS) and the U 5f → U 5d RXES permits the exploration of the uranium outer valence molecular orbital formation.

EXPERIMENTAL PROCEDURE

NEXAFS and RXES spectra were collected at undulator Beamline 7.0.1 of the Advanced Light Source (ALS) at the Ernest O. Lawrence Berkeley National Laboratory (LBNL).^{10,11} Experiments were done in the XES branchline chamber at approximately 5×10⁻⁹ Torr. The RXES spectra were measured with the beam incident at ~75° to the substrate normal. A grazing-incidence fluorescence grating spectrometer was used to measure the RXES spectra and energies were calibrated to the elastic scattering features.^{12,13} NEXAFS spectra were collected in the total yield mode with the beam incident normal to the substrate.

All uranium materials used in this study were depleted. The samples of carbon-coated uranium metal and U₆Nb alloy were prepared at the Lawrence Livermore National Laboratory as discs of ~5 mm diameter and transported under vacuum to limit surface oxidation. The UO₂, UF₄, UF₅, U₃O₈, and UO₃ samples were prepared at LBNL by pressing powders into indium.

RESULTS AND DISCUSSION

The U 5d total electron yield NEXAFS spectra of carbon-coated uranium metal, UO₂, U₃O₈, and UO₃ are shown in Figure 1A and agree with previously obtained results.^{13,14} The bars schematically identify the U 5d_{5/2,3/2} binding energies (O₄ and O₅ thresholds) for α-U and the

uranium oxide materials on the basis of the XPS data.^{14,15} The NEXAFS spectra of the uranium metal and the uranium oxides differ greatly. For example, in the spectrum of UO_3 as well as uranium metal, there is a shoulder at ~ 108 eV, which is absent in the spectra of UO_2 and U_3O_8 . This indicates the presence of uranyl compounds (hydroxides and carbonates) on the metal surface. Thus, the feature at ~ 108 eV is a transition to an orbital formed in the uranyl group (UO_2^{2+}). The shoulder at ~ 101.5 eV in the spectrum of uranium metal is similar to that from UO_2 and is explained by the presence of an oxide layer on the metal surface. The features of the NEXAFS spectra were used to determine the excitation energies for the RXES measurements.

RXES spectra were collected from the uranium materials at the excitation energies indicated by arrows in the NEXAFS spectra of Figure 1A. The spectral information obtained from these studies at the various photon energies is summarized in Table 1. Features with a spin-orbit splitting of ~ 10 eV are the transitions $\text{U } 5f \rightarrow \text{U } 5d_{5/2,3/2}$. Figure 1B is representative of the quality of XES spectra (except that most spectra span ~ 25 eV) and shows the spectra collected at the excitation energy A from U, UO_2 , UF_4 , UF_5 , U_3O_8 , and UO_3 . The features in these spectra are attributed to the ff -excitation process and agree with earlier results. As expected, the ff -excitation peaks are stronger in materials with ionic bonding like UO_2 , UF_5 , and especially UF_4 . The features in the spectrum of uranium metal are similar to those in UO_2 again indicating the presence of UO_2 on the surface. Figure 1B highlights the spectral differences in the uranium materials, that is evidence for differences in the formation of the electronic structures. For more reliable and accurate interpretation of the ff -excitation process in uranium compounds, detailed theoretical calculations of the valence band structure taking into account many body and charge transfer effects must be carried out.

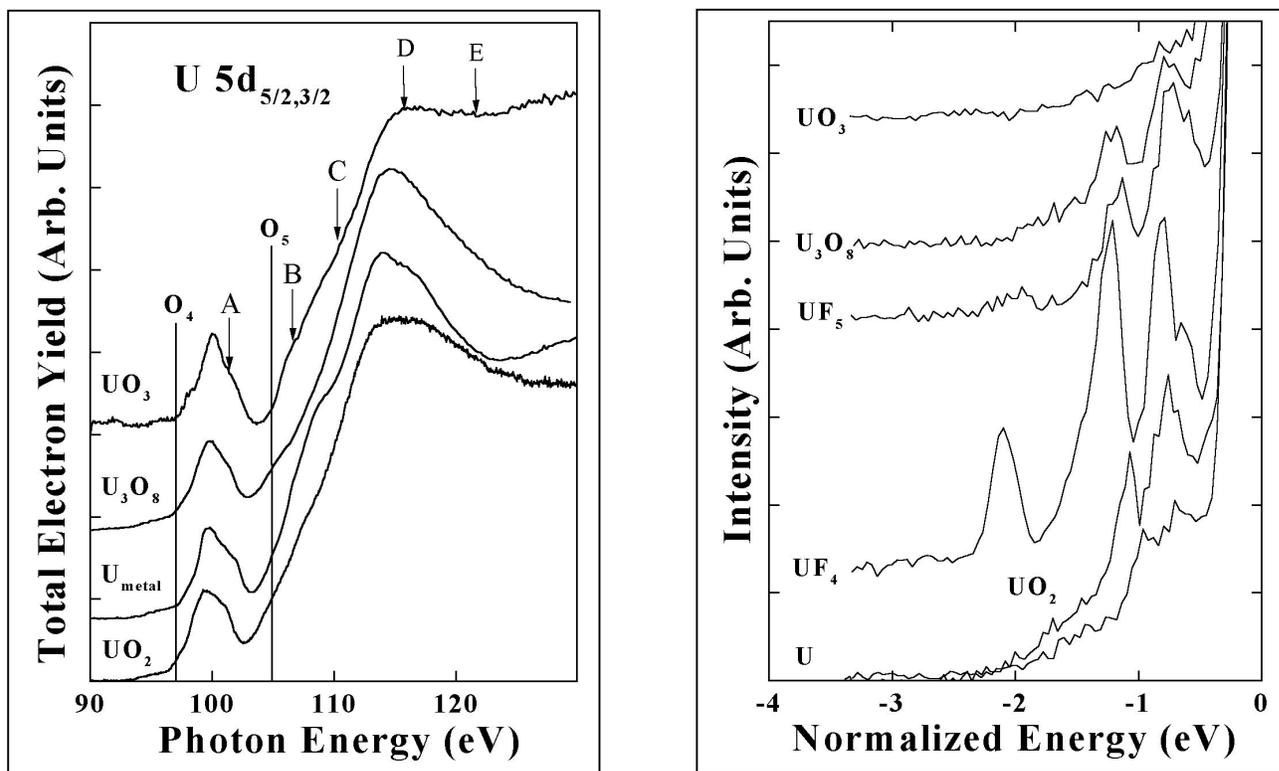


Figure 1. (A-left panel) Total electron yield NEXAFS spectra of carbon coated uranium metal, UF_4 , UF_5 , UO_2 , U_3O_8 , and UO_3 . Intensities normalized to the peak at ~ 100 eV. Arrows indicate the excitation energies for RXES spectra. (B-right panel) RXES spectra showing ff -excitation process in U, UO_2 , UF_4 , UF_5 , U_3O_8 , and UO_3 collected with excitation energy A. Energies are aligned relative to the elastic scattering peaks. Intensities are normalized to the elastic scattering peaks.

Table I. Resonant soft x-ray emission transitions and energies in eV for metallic uranium, UO₂, UF₄, UF₅, U₃O₈, and UO₃.

Peak	Transition	U _{metal}	UO ₂	UF ₄	UF ₅	U ₃ O ₈	UO ₃
1	5d _{5/2} ←5f	89.9	91.0	90.4	90.9	91.6	91.6
2	5d _{3/2} ←5f	100.8	100.3	100.0	100.3	100.8	100.8
3	5d _{3/2} ←OVMO	105.5	105.5	104.7	106.3	105.9	105.9
4	5d _{3/2} ←OVMO	107.4	107.9	---	---	108.2	108.2
5	5d _{3/2} ←OVMO	110.4	111.8	109.5	111.7	---	---
IS	OVMO→OVMO	---	---	---	---	4.2*	4.0*

*Distance from the elastic scattering peak.

The RXES spectra collected at excitation energy B (not shown) show significant differences between U, UF₄, and the uranium oxides. The U 5f → U 5d_{3/2} transition does not occur at this energy. This indicates that electrons from U 5d_{3/2} core level are not promoted to U 5f level directly, but to another valence orbital formed from the interaction of U 5f, 6s, 6d – O 2p electrons. This is then followed by the U 5f →U 5d_{3/2} transition. Apparently such orbitals do not form in U and UF₄ or the excitation energy is insufficient to promote the U 5d_{3/2} electrons to a more energetic orbital. This demonstrates the difference in formation of the MO system for uranium with oxygen and non-oxygen ligands.

Inelastic scattering features are also observed in the RXES spectra and are especially evident in the UO₃ spectra. This process occurs when part of excitation photons lose energy to promote electrons from one valence molecular orbitals to a higher one. This transition is associated with the participation of the OVMO formed in the uranyl group UO₂²⁺. A similar process is evident in the XPS spectrum of UO₃.⁵ Thus, the XPS spectrum of the U 4f_{7/2} electrons has a satellite located at 3.9 eV from the basic line.⁵ This satellite forms due to the dynamic effect, when photoelectrons escaping the sample lose a part of their energy to excite electrons from a valence orbital to a higher one. This demonstrates the complementary nature of the XPS and RXES results. The same inelastic scattering takes place in U₃O₈, but not in uranium metal, UF₄, UF₅, or UO₂. This demonstrates the difference in the electronic structure of the OVMO in uranium and its compounds.

CONCLUSION

RXES has proven to be an effective tool to study of the electronic structure of uranium compounds. The structure of the RXES spectra shows a strong resonant behavior and dependence on the localization of the U 5f electrons. The spectral structures of the uranium compounds investigated are differ significantly and can be interpreted by the formation of the outer valence molecular orbitals from the interaction of the U 5f, 6s, 6d, and O 2p electrons. The RXES spectra were interpreted in the one-electron MO LCAO (molecular orbitals as linear combinations of atomic orbitals) approximation. These considerations are valid provided the formed molecular orbitals retain their partial atomic nature. For a more reliable and accurate interpretation of the RXES spectra of uranium compounds, precise and detailed theoretical calculations of the valence band electron structure taking into account many body and charge transfer effects, have to be carried out.

ACKNOWLEDGEMENTS

The authors thank and recognize George Meigs for experimental assistance and Keith Heinzelman for providing safety support during the experiments.

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This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials and Chemical Sciences Divisions, of the U.S. Department of Energy under contract No. DE-AC03-76SF00098. This work also was supported in part by the Laboratory Directed Research and Development program at the Ernest O. Lawrence Berkeley National Laboratory.

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